[Claim(s)]

[Claim 1] A ** of composition which is shown by Formula (1):M1aM2 and fills 0.25<=a<3, and formula (2):M1 -- [it is shown by 'bM2' and] Are B ** of composition which fills 1<=b and a<b the active material which it has, and [M1 and M1'] Na, K, Rb, Cs, Cs, Ti, Zr, Hf, V, Nb, Ta, Cs, Sr, Ba, Y, La, Cr, Mo, W, Mn, Tc, Ru, Are at least one sort of elements chosen from the group which consists of Os, Co, Rh, Ir, nickel, Pd, Cu, Ag, and Fe (m1), and [M2 and M2'] The **** active material for nonaqueous electrolyte rechargeable batteries characterized by being at least one sort of elements chosen from the group which consists of aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi (m2).

[Claim 2] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 which consists of 0 to 50 weight % of ** other than 20 to 80 weight % of A **, 20 to 80 weight % of B **, A **, and B **.

[Claim 3] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 or 2 which 80weight % or more of A ** is distributing in the matrix of B ** where B ** is contacted.

[Claim 4] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 to 3 which one of ** of A ** and B ** are distributing to island shape with an average particle diameter of 0.05-20 micrometers in the matrix of ** of another side, or both A ** and B ** become from a particle with an average particle diameter of 1-20 micrometers, respectively.

[Claim 5] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 to 4 in which A ** and B ** have the lamellar structure which became intricate mutually.

[Claim 6] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 to 5 whose average cross-section area of the crystal grain of A ** and B ** observed in arbitrary sections is two or less ten to 7 cm.

[Claim 7] The **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 whose average particle diameter of an active material is 45 micrometers or less.

[Claim 8] The manufacturing process of the **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 to 7 characterized by compounding by the plasma method, the atomizing method, the rapid cooling method, the casting process, the mechanical alloy method, or the mechanochemical method.

[Claim 9] The simple substance of various materials elements is mixed by mass and ratios tabular or granular, and arbitrary. The process cast in an arc melting furnace, and the obtained casting arcas Under argon atmosphere. The manufacturing process of the **** active material for nonaqueous electrolyte rechargeable batteries according to claim 1 to 7 characterized by having the process made into spherical particles by the gas atomizing method by diameter of injection nozzle 0.5-5mmphi, the injection pressure 50 - 300 kgf/cm2.

[Claim 10] The nonaqueous electrolyte rechargeable battery possessing the plus terminal in which charge and discharge are possible, nonaqueous electrolyte, and *** which consists of a *** active material according to claim 1 to 7.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the *** active material for nonaqueous electrolyte rechargeable batteries, its manufacturing process, and a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte rechargeable battery which makes lithium or a lithium compound *** can expect the high voltage and high energy density, and many researches are done. The oxide of a transition metal and a chalcogen compound, for example, LiMn2O4, LiCoO2, LiNiO2, V2O5, Cr2O5, MnO2, TiS2, MoS2, etc. are known by the plus terminal active material of the nonaqueous electrolyte rechargeable battery. These have stratified structure or tunnel structure, and have the crystal structure which a lithium ion can frequent.

[0003] On the other hand, as a *** active material, metal lithium is examined widely and is. However, when metal lithium is used, it deposits on the lithium surface at the time of charge, tree-like lithium, i.e., a DENDO light, and there is a problem of producing an internal short circuit in contact with a fall or plus terminal of charge-and-discharge efficiency. Then, tree-like growth of lithium is controlled and examination which uses lithium for a *** active material for occlusion and the lithium system alloy which can be emitted, for example, a lithium aluminum alloy etc., is made. However, if deep charge and discharge are repeated, electrode material will fine-powder and a problem will arise in the cycle characteristic.

[0004] While capacity is smaller than metal lithium and a lithium system alloy, the lithium ion battery used for *** is reversibly put [carbon material / occlusion and / which could emit and was excellent in the cycle characteristic, safety, etc. / black lead system] in practical use in lithium now. However, when a black lead system carbon material is used for ***, the practical capacity is 350 mAh/g near theoretical capacity (372 mAh/g). Moreover, theoretical density is low in cc and 2.2g /, and if it is actually sheet-like ***, density will fall further. Therefore, in order to ask for the further high capacity-ization of a battery, it is necessary to use metal system inorganic matter material with high capacity per unit volume for a *** active material.

[0005]

[Problem to be solved by the invention] a repetition of the expansion accompanying [when

metal system inorganic matter material is used for a **** active material } the occlusion of lithium and discharge, and contraction -- an active material -- fine -- powdering arises. Other active materials or a physical point of contact with an electric conduction agent is lost in ****, and the fine-powdered active material serves as inactivity seemingly, and becomes the big factor of capacity reduction from electronic conduction nature being lost.

[0006] Then, ** which carries out occlusion of the lithium into 1 particles, and ** which does not carry out occlusion are made to live together. The technology which eases the stress of a charge state (occlusion state) by ** which does not absorb lithium (JP,H11-86854,A). Two or more ** of ** which carry out occlusion of the lithium into 1 particles are made to live together the technology (JP,H11-86853,A) which eases the stress by the structural change at the time of the lithium occlusion of each ** is indicated, and it is said by making crystal size detailed that the effect of stress relaxation improves. However, the effect is insufficient.

[0007] Two or more ** are made to live together in active material particles, and even if it makes crystal size detailed and misses expansion stress to ****, when the rates of expansion of each ** differ greatly, the stress in active material particles becomes uneven, for this reason, a part of [with large expansion stress] ** -- fine -- powdering takes place and it is thought that it is isolated from active material particles. When ** of 1 is the simple substance of lithium and the element which is easy to alloy, the tendency which said phenomenon produces is still larger.

[0008]

[Means for solving problem] this invention is followed on expansion and contraction of a **** active material -- fine -- it aims at reconciling the high capacity and the long-life life of a battery by controlling powdering. namely, -- this invention -- a formula -- (-- one --) -- : -- M -- one -- aM -- two -- being shown -- having -- 0.25 -- <= -- a -- < -- three -- filling -- composition -- A -- ** -- and -- a formula -- (-- two --) -- : -- M -- one -- ' -- bM -- two -- ' -- being shown -- having -- Are B ** of composition which fills 1<=b and a<b the active material which it has, and [M1 and M1'] Na, K, Rb, Cs, Ce, Ti, Zr, Hf, V, Nb, Ta, Ca, Sr, Ba, Y, La, Cr, Mo, W, Mn, Tc, Ru, Are at least one sort of elements chosen from the group which consists of Os, Co, Rh, Ir, nickel, Pd, Cu, Ag, and Fe (m1), and [M2 and M2'] It is related with the **** active material for nonaqueous electrolyte rechargeable batteries characterized by being at least one sort of elements chosen from the group which consists of aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi (m2).

[0009] As for said active material, it is desirable to consist of 0 to 50 weight % of ** other than 20 to 80 weight % of A **, 20 to 80 weight % of B **: A **, and B **. Moreover, it is desirable to have the interface which A ** and B ** contacted. Moreover, it is desirable that 50weight % or more of A ** is distributing in the matrix of B ** where B ** is contacted. Moreover, one of ** of A ** and B ** are distributing to island shape with an average particle diameter of 0.05-20 micrometers in the matrix of ** of another side, or it is desirable that both A ** and B ** have

the shape of a particle with an average particle diameter of 1-20 micrometers, respectively Moreover, it is desirable that A ** and B ** have the lamellar structure which became intricate mutually Moreover, the 1.5 or more aspect ratio thing which at least one ** of A ** and B ** is distributing needlelike is desirable. Moreover, it is desirable that the average cross-section area of the crystal grain of A ** and B ** observed in arbitrary sections is two or less ten to 7 cm. Moreover, as for the average particle diameter of said active material, it is desirable that it is 45 micrometers or less.

[0010] In said active material, A ** are at least one sort of ** chosen from the group which consists of NaSn2, KSn2, SrSn3, BaSn3, LaSn2, CeSn3, ZrSn2, MnSn2, CoSn2, PdSn2, and FeSn2, and B ** Na2Sn, KSn, La2Sn, Zr3Sn2, Zr4Sn, V3Sn, Nb3Sn, Ta3Sn, MnSn, Mn2Sn, Mn3Sn, FeSn, Fe1.3Sn, Fe3Sn, It is desirable that they are at least one sort of ** chosen from the group which consists of CoSn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu6Sn5, Cu3Sn, Cu4Sn, Ti6Sn5, and Ti2Sn.

[0011] A ** in said active material Moreover, NaSn, KSn, FeSn, They are at least one sort of ** chosen from the group which consists of CoSn and PdSn. B ** Na2Sn, La2Sn, Zr3Sn2, Zr4Sn, V3Sn, It is desirable that they are at least one sort of ** chosen from the group which consists of Nb3Sn, Ta3Sn, Mn2Sn, Mn3Sn, Fe1.3Sn, Fe3Sn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu6Sn5, Cu3Sn, Cu4Sn, Ti6Sn5, and Ti2Sn.

[0012] Moreover, they are at least one sort of ** chosen from the group which A ** becomes from Ti6Sn5 and Cu6Sn5 in said active material, B ** Na2Sn, La2Sn, Zr3Sn2, Zr4Sn, V3Sn, it is desirable that they are at least one sort of ** chosen from the group which consists of Nb3Sn, Ta3Sn, Mn2Sn, Mn3Sn, Fe1.3Sn, Cu3Sn, Fe3Sn, Fe6Sn, Fe12Sn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu4Sn, and Ti2Sn

[0013] A ** in said active material Moreover, Na2Sn, K2Sn, Mg2Sn, They are at least one sort of ** chosen from the group which consists of Ca2Sn, SrSn, Ba2Sn, La2Sn, and Ti2Sn. It is desirable that B ** are at least one sort of ** chosen from the group which consists of Mn3Sn, Fe3Sn, Fe6Sn, Fe12Sn, nickel3Sn, nickel6Sn, Cu3Sn, Cu4Sn, and Ti2Sn

[0014] Moreover, in said active material [A **] NaSi2, CaSi2, SrSi2, BaSi2, YSi2, LaSi2, CeSi2, TiSi2, ZrSi2, VSi2, NbSi2, TaSi2, CrSi2, MoSi2, WSi2, MnSi2, CoSi2, CuSi2, FeSi2 And they are at least one sort of ** chosen from the group which consists of NiSi2, B ** NaSi KSi, Mg2Si, Ca2Si, Ce2Si, TiSi, Ti5Si3, ZrSi, V3Si, Nb5Si3, Ta2Si, CrSi, Cr2Si, Mo3Si, W3Si2, MnSi, Mn5Si3, Mn3Si, It is desirable that they are at least one sort of ** chosen from the group which consists of FeSi, Fe5Si3, FeSi2, CoSi, Co2Si, Co3Si, NiSi, nickel3Si2, nickel2Si, CuSi, Cu5Si5, Cu3Si, and Cu4Si.

[0015] A ** in said active material Moreover, NaSi, KSi, CaSi, BaSi, TiSi, ZrSi, CrSi, MnSi, FeSi, CoSi, They are at least one sort of ** chosen from the group which consists of PdSi, NiSi, and CuSi. B ** Mg2Si, Ca2Si, Ce2Si, Ti5Si3, V3Si, Nb5Si3, Ta2Si, Cr2Si, Mo3Si, W3Si2,

Mn5Si3, Mn3Si. It is desirable that they are at least one sort of ** chosen from the group which consists of Fe5Si3, Fe3Si, Co2Si, Co3Si, nickel3Si2, nickel2Si, Cu5Si5, Cu3Si, and Cu4Si.

[0015] Moreover, they are at least one sort of ** chosen from the group which A ** becomes from Ti5Si3, Nb5Si3, W5Si2, Mn5Si3, Fe5Si3, and Cu5Si5 in said active material. It is desirable that B ** are at least one sort of ** chosen from the group which consists of Mg2Si, Ca2Si, Ce2Si, V3Si, Ta2Si, Cr2Si, Mo3Si, Mn3Si, Fe3Si, Co2Si, Co3Si, nickel2Si, Cu3Si, and Cu4Si.

[0017] A ** in said active material Moreover, Mg2Si, Ca2Si, SrSi, They are at least one sort of ** chosen from the group which consists of Ce2Si, Cr2Si, Co2Si, Pd2Si, and Cu2Si. It is desirable that B ** are at least one sort of ** chosen from the group which consists of V3Si, Mo3Si, Mn3Si, Fe3Si, Co2Si, Cu3Si, and Cu4Si.

[0018] Moreover, in said active material [A **] CaAl4, CaAl2, SrAl4, BaAl4, BaAl2, LaAl4, LaAl2, CeAl4, CeAl2, TiAl3, ZrAl3, ZrAl2, VAl3, V5aluminum5, NbAl3, TaAl3, CrAl4, MoAl2, WAl4, MnAl4, They are at least one sort of ** chosen from the group which consists of MnAl3, Co2aluminum5, CuAl2, FeAl3, FeAl2, NiAl3, and nickel2aluminum3. B ** SrAl, BaAl, LaAl, La<SUB>3aluminum2, CeAl, it is desirable that they are at least one sort of ** chosen from the group which consists of Ca3aluminum2, TiAl, ZrAl, Zr2aluminum, Mg3aluminum, MnAl, FeAl, Fe3aluminum, CoAl, NiAl, CuAl, and Cu4aluminum3.

[0019] A ** in said active material Moreover, SrAl, BaAl, LaAl, They are at least one sort of ** chosen from the group which consists of CeAl, TiAl, ZrAl, MnAl, FeAl, CoAl, NiAl, and CuAl. It is desirable that B ** are at least one sort of ** chosen from the group which consists of La3aluminum2, Ca3aluminum2, Zr2aluminum, Mg3aluminum, Fe3aluminum, and Cu4aluminum3.

[0020] Moreover, this invention relates to the manufacturing process of said active material characterized by compounding by the plasma method, the atomizing method, the rapid cooling method, the casting process, the mechanical alloy method, or the mechanochemical method. Moreover, this invention mixes the simple substance of various materials elements by mass and ratios tabular or granular, and arbitrary. It is related with the manufacturing process of said active material characterized by having the process cast in an arc melting furnace, and the process which makes spherical particles the obtained casting article by the gas atomizing method under argon atmosphere by diameter of injection nozzle 0.5-5mm/phi, the injection pressure 50 - 300 kg/cm2. Furthermore, this invention relates to the nonaqueous electrolyte rechargeable battery possessing the plus terminal in which charge and discharge are possible, nonaqueous electrolyte, and *** which consists of said active material. In addition, in this invention, an active material means the material which contains an activity portion electrochemically, and the material containing an inactivity portion is also included in an active material.

[0021]

[Mode for carrying out the invention] the active material of this invention is shown by formula (1).M1aM2 -- 0.25<=a<3, A ** of composition which fills 0.5<=a<=2 preferably, and formula (2)M1 -- it is shown by 'bM2' and has 1<=b and a<b, and B ** of composition that fills 1<=b<=5 and a<b preferably, the case where an active material has A ** and B ** -- an active material -- fine -- powdering is controlled and degradation of the battery by a charge-and-discharge cycle is suppressed. Since the difference of the expansion stress at the time of the lithium occlusion of A ** and that of B ** is small, this is considered because the expansion stress in the whole active material is eased uniformly. Among a formula (1), if the expansion stress of A ** is very large when a is smaller than 0.25, and it becomes easy to powder fine and it becomes three or more, a unit weight and the amount of Li reactions per volume will become small too much, and will turn into low capacity. Moreover, if the expansion stress of B ** will also become large, both ** will expand among a formula (2), if b becomes less than one, and 5 is exceeded, the stress difference of A ** and B ** will become intense. Moreover, relief of the expansion stress by making two or more ** which carry out occlusion of the lithium exist. As for a and b, from balance with equalization of the expansion stress in the whole active material by making small the difference of the expansion stress of A **, and that of B ** etc., it is desirable to fill 1<(b/a) <10 and also 1.5 <=(b/a) <=5.

[0022] [M1 and M1'] among a formula (1) and a formula (2) They are at least one sort of elements chosen from the group which consists of Na, K, Rb, Cs, Ce, Ti, Zr, Hf, V, Nb, Ta, Ca, Sr and Ba, Y, La, Cr, Mo, W, Mn, Tc, Ru, Os, Co, Rh, Ir, nickel, Pd, Cu, Ag, and Fe (m1). Although two or more elements may be contained, as for ** of 1, it is desirable to consist of an element chosen from one sort of groups (M1). When A ** and B ** consist of an element chosen from one sort of groups (m1), respectively, it is desirable also in a group (m1) to consist of Ti, Zr, Sr, Ba, Mn, Co, nickel, and Cu or Fe, and it is especially desirable to consist of Ti, Mn, Co, Cu, or Fe.

[0023] M2 and M2' are at least one sort of elements chosen from the group which consists of aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi (m2) among a formula (1) and a formula (2). Although two or more elements may be contained, as for ** of 1, it is desirable to consist of an element chosen from one sort of groups (m2). When A ** and B ** consist of an element chosen from one sort of groups (m2), respectively, it is desirable also in a group (m2) to consist of aluminum, In, Si, germanium, and Sn or Pb, and consisting of aluminum, Si, or Sn is especially desirable.

[0024] As for the active material which has A ** and B **, it is desirable to consist of 0 to 50 weight % of ** other than 20 to 80 weight % of B **, further 40 to 70 weight %, A **, and B ** and further 5 to 30 weight % 20 to 80 weight % of A ** and further 30 to 60weight %. Moreover it is desirable to have the interface which A ** and B ** contacted. The contact interface of A **

and B ** is for playing a role important for the stress relaxation at the time of lithium occlusion, or reservation of the lithium channels of communication in active material particles. Therefore, more ones of a contact interface are desirable, for example, it is desirable that 50weight % or more of A ** is distributing where B ** is contacted into the matrix of B **. Moreover, when one of ** of A ** and B ** are distributing to island shape in the matrix of ** of another side, Or when both A ** and B ** are distributing to island shape, respectively, or when it consists of particles, as for the average particle diameter of an island and particles, it is desirable respectively 0.05-20 micrometers, further 0.1-5 micrometers, and that further 1-20-micrometer 0.1-20 micrometers are 1-5 micrometers especially. Here, said average particle diameter is called for from the average of the diameter of the section of the island observed in the section obtained when active material particles are cut in respect of being arbitrary, for example, or particles. Furthermore, as desirable structure, the lamellar structure to which A ** and B ** became intricate mutually, i.e., the structure with which the active material section became entangled mutually like meshes of a net, is mentioned. In order to acquire lamellar structure, it is necessary to compound and heat-treat, for example by a rapid cooling method like a roll rapid cooling method or the atomizing method, making smaller the difference of the expansion stress of A **, and that of B ** -- an active material -- fine -- in order to control powdering still more efficiently, the 1.5 or more-aspect ratio thing which at least one ** of A ** and B ** is distributing needlelike is desirable. Here, it asks from the length of the section of needlelike particles and the average of the ratio of width which are observed in the section obtained when an aspect ratio means the ratio of the length of needlelike particles, and Haba, for example, active material particles are cut in respect of being arbitrary.

[0025] As for the average particle diameter of the crystal grain which constitutes A ** and B **, it is desirable that they are 13 micrometers or less and further 0.1-5 micrometers. If said average particle diameter exceeds 13 micrometers, there will be a tendency for the crystal grain itself to be ground by expansion stress at the time of lithium occlusion, and it will become easy to powder an active material fine. Moreover, as for the average cross-section area of the crystal grain of A ** and B ** observed in arbitrary sections, it is desirable that it is two or less ten to 7 cm, and further 10-9 - 10-8cm2. Moreover, since **** of a nonaqueous electrolyte rechargeable battery generally has the shape of an about 80-micrometer sheet, as for the average particle diameter of active material particles, it is desirable that they are 45 micrometers or less and further 5-30 micrometers. When particle diameter exceeds 40 micrometers, unevenness increases in the surface of sheet-like **** and there is a tendency for the battery characteristic to fall.

[0026] this invention -- an active material -- inside -- **** -- A -- ** -- B -- ** -- others -- further -- using another -- ** -- for example, -- a formula -- : -- M -- one -- " -- xM -- two -- " -- being shown -- having -- bx -- filling -- composition -- ** -- etc. -- existing -- **** . M1" is at least one

sort of elements chosen from the aforementioned (m1) group here, and M2" is at least one sort of elements chosen from the aforementioned (m2) group. Moreover, one or more sorts of ** which consist only of an element chosen from the group, for example (m1) may exist. In this case, although electric discharge capacity decreases slightly, it becomes possible { obtaining still longer lasting active material particles }. Moreover, although ** which consists only of an element chosen from the group (m2) may also exist, it is desirable that it is 10 or less weight % on the characteristic of a battery and in all the active materials.

[0027] A ** in said active material independent or when { of Na8Sn2, K5Sn2, Sr5Sn3, Ba5Sn3, La5Sn2, Ce5Sn3, Zr5Sn2, Mn5Sn2, Co5Sn2, Pd5Sn2, or Fe5Sn2 } it is two or more sorts. B ** Na2Sn, K3Sn, Ca2Sn, Zr3Sn2, Zr4Sn, V3Sn, Nb3Sn, Ta3Sn, Mn3Sn, Mn2Sn, Mn3Sn. It is desirable independent or that they are two or more sorts of FeSn, Fe1.3Sn, Fe3Sn, Co3Sn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu6Sn5, Cu3Sn, Cu4Sn, Ti6Sn5, or Ti2Sn.

[0028] Moreover, that Na5Sn, K3Sn, Fe5Sn, Co5Sn, or Pd5Sn is independent or when it is two or more sorts. A ** in said active material { B ** } Na2Sn, La2Sn, Zr3Sn2, Zr4Sn, V3Sn, Nb3Sn. It is desirable independent or that they are two or more sorts of Ta3Sn, Mn2Sn, Mn3Sn, Fe1.3Sn, Fe3Sn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu6Sn5, Cu3Sn, Cu4Sn, Ti6Sn5, or Ti2Sn.

[0029] Moreover, independent or when { of Ti6Sn5 or Cu6Sn5 } it is two sorts, A ** in said active material { B ** } Na2Sn, La2Sn, Zr3Sn2, Zr4Sn, V3Sn, Nb3Sn. It is desirable independent or that they are two or more sorts of Ta3Sn, Mn2Sn, Mn3Sn, Ti3Sn, Cu3Sn, Fe3Sn, Fe6Sn, Fe12Sn, Co3Sn2, nickel3Sn2, nickel3Sn, Cu6Sn, or Ti2Sn.

[0030] A ** in said active material Moreover, Na2Sn, K2Sn, Mg2Sn, That Ca2Sn, Sr2Sn, Ba2Sn, La2Sn, or Ti2Sn is independent or when it is two or more sorts, { B ** } It is desirable independent or that they are two or more sorts of Mn2Sn, Fe2Sn, Fe6Sn, Fe12Sn, nickel3Sn, nickel6Sn, Cu3Sn, Cu4Sn, or Ti3Sn.

[0031] Moreover, in said active material { A ** } NaSi2, CaSi2, SrSi2, BaSi2, VSi2, LaSi2, CeSi2, TiSi2, ZrSi2, VSi2, NbSi2, TaSi2, CrSi2, MoSi2, WSi2, MnSi2, CeSi2, CuSi2, FeSi2 Or independent or when { of NiSi2 } it is two or more sorts, { B ** } NaSi, KSi, Mg2Si, Ca2Si, Ce2Si, TiSi, TiSi3, ZrSi, VSi, NbSi3, Ta2Si, CrSi, Cr2Si, Mo3Si, WSi2, MnSi, Mn5Si3, Mn3Si, It is desirable independent or that they are two or more sorts of FeSi, Fe5Si3, Fe2Si, CoSi, Co2Si, Ce3Si, MiSi, nickel3Si2, nickel2Si, CuSi, Cu6Si5, Cu3Si, or Cu4Si.

[0032] A ** in said active material Moreover, NaSi, KSi, CaSi. That BaSi, TiSi, ZrSi, CrSi, MnSi, FeSi, CoSi, PdSi, NiSi, or CuSi is independent or when it is two or more sorts. { B ** } Mg2Si, Ca2Si, Ce2Si, Ti5Si3, V2Si, Mo5Si3, Ta2Si, It is desirable independent or that they are two or more sorts of Cr2Si, Mo3Si, W5Si3, Mn5Si3, Mn2Si, Fe5Si3, Fe3Si, Co2Si, Co6Si, nickel3Si2, nickel2Si, Cu6Si5, Cu3Si, or Cu4Si.

[0033] Moreover, independent or when { of Ti5Si3, Nb5Si3, W5Si2, Mn5Si3, Fe5Si3, or Cu6Si5 } it is two or more sorts, A ** in said active material { B ** } It is desirable independent

or that they are two or more sorts of Mg2Si, Ca2Si, Ce2Si, V3Si, Ta2Si, Cr2Si, Mo3Si, Mn3Si, Fe3Si, Co2Si, Os3Si, nickel2Si, Cu3Si, or Cu4Si.

[0034] A "" in said active material Moreover, Mg2Si, Ca2Si, SrSi, That Ce2Si, Cr2Si, Co2Si, Pd2Si, or Cu2Si is independent or when it is two or more sorts, as for B "", it is desirable independent or that they are two or more sorts of V3Si, Mo3Si, Mn3Si, Fe3Si, Os3Si, Cu3Si, or Cu4Si.

[0035] Moreover, in said active material [A""] CaAl4, CaAl2, SrAl4, BaAl4, BaAl2, LaAl4, LaAl2, CeAl4, CeAl2, TiAl3, ZrAl3, ZrAl2, VAl3, V(aluminum)3, NbAl3, TaAl3, CrAl4, MoAl3, WAl4, MnAl4, Independent or when [of MnAl3, Co2aluminum5, CuAl2, FeAl3, FeAl2, NiAl3 or Nickel2aluminum3] it is two or more sorts, It has desirable B "" independent or that they are two or more sorts of SrAl, BaAl, LaAl, La3aluminum2, CeAl, Ce3aluminum2, TiAl, ZrAl, Zr2aluminum, Mo3aluminum, MnAl, FeAl, Fe3aluminum, CoAl, NiAl, CuAl, or Cu4aluminum3.

[0036] A "" in said active material Moreover, SrAl, BaAl, LaAl, That CeAl, TiAl, ZrAl, MnAl, FeAl, CoAl, NiAl, or CuAl is independent or when it is two or more sorts, as for B "", it is desirable independent or that they are two or more sorts of La3aluminum2, Ce3aluminum2, Zr2aluminum, Mo3aluminum, Fe3aluminum, or Cu4aluminum3.

[0037] The active material concerning this invention can mix the simple substance of various materials elements by mass and ratios tabular or granular, and arbitrary, for example, and can compound it by being independent, or combining the method, for example, the plasma method, of performing predetermined heat treatment, the atomizing method, a rapid cooling method, or a casting process, and using it. Moreover, otherwise, it is compoundable by the mechanical alloy method and the mechanochemical method. According to said plasma method, very small particles are easy to be obtained, according to said atomizing method, very small spherical particles are easy to be obtained, and mass-production nature is good, according to said rapid cooling method, the particles of a very small organization are easy to be obtained, and according to said casting process, composition is easy. According to said mechanical alloy method or said mechanochemical method, very small particles and a detailed organization can be realized. As a manufacturing process of said more desirable active material, for example [the simple substance of various materials elements] The manufacturing process which consists of a process which mixes by mass and ratios tabular or granular and arbitrary, and is cast in an arc melting furnace, and a process which makes spherical particles the obtained casting article by the gas atomizing method under argon atmosphere by diameter of injection nozzle 0.5-5mmphi, the injection pressure 50 - 300 kgf/cm2 is mentioned.

[0038] The nonaqueous electrolyte rechargeable battery of this invention can be obtained, if "" is produced by a general method using said active material and it combines with the plus terminal and nonaqueous electrolyte in which charge and discharge are possible.

[0039]

[Working example] Next, although this invention is explained still more concretely based on a work example, these do not limit this invention.

<<Work examples 1-65>> ** which consists only of an element which has the active material composition (composition of a materials element) shown in Tables 1-3, and was chosen from A **, B **, and a group (m2) (all over Table 1-3, it is indicated as C **.) In addition, it sets to the sequence of C ** and the numerical value in ( ) shows weight % of C ** in an active material. the same in Table 4 -- and other ** (the display "-" in the sequence of other ** does not mean that other ** do not exist among Table 1-3.) the same in Table 4. from -- each becoming active material was prepared in the following procedures. It mixed by mass and ratios tabular or granular, and arbitrary, and the simple substance of various materials elements was cast in the arc melting furnace. The obtained casting article was made into spherical particles under argon atmosphere using the gas atomizing method. At this time, the diameter of an injection nozzle was 1mmphi, and injection pressure was 100kg/cm2. Through and an active material particle with an average particle diameter of 28 micrometers were obtained for the sieve of the 45-micron mesh to the obtained particles.

[0040] What analyzes the obtained active material particles according to an X diffraction, consists of two or more ** shown in Table 1, and consists of 20 to 85 weight % of A **, 30 to 70 weight % of B **, 0 to 10 weight % of ** (C **) that consist only of an element chosen from the group (m2), and 0 to 20 weight % of other ** was chosen. When surface analysis by ESMA was conducted to the selected active material particles, the average particle diameter of the crystal grain of every active material particle was within the limits of 0.3-13 micrometers. Moreover, the average cross-section area of the crystal grain which constitutes A ** and B ** was 5x10-8cm2 at the maximum.

[0041]

[Table 1]

[illegible]	[illegible]	A[illegible]	B[illegible]	C[illegible]	[illegible]	[illegible] (mAh/g)	[illegible] (%)
1	FeSn	$FeSn_2$	CoSn	-	-	750	78
2	$Fe_{1.3}Sn$	$FeSn_2$	FeSn	Sn(β)	-	820	71
3	Fe_2Sn_3	$FeSn_2$	FeSn, Fe_3Sn	-	-	640	88
4	Fe_3Sn	$FeSn_2$	FeSn, Fe_3Sn	-	Fe	510	94
5	CoSn	$CoSn_2$	CoSn	-	-	770	75
6	Co_2Sn	$CoSn_2$	CoSn	-	Co	520	91
7	$CoSn_2$	$CoSn_2$	CoSn	Sn(β)	-	800	88
8	NiSn	$NiSn_2$	Ni_3Sn	-	-	620	81
9	Ni_3Sn	$NiSn_2$	Ni_3Sn_2, Ni_3Sn	-	-	590	94
10	$Ni_{1.5}Sn$	$NiSn_2$	Ni_3Sn, Ni_3Sn	-	Ni	560	57
11	Ni_3Sn_2	$NiSn_2$	Ni_3Sn	Sn(β)	-	780	77
12	$FeNiSn_2$	$FeSn_2$, $NiSn_2$	FeSn, Ni_3Sn	-	Fe	730	81
13	ZrSn	$ZrSn_2$	Zr_5Sn_3	-	-	700	80
14	$FeZrSn_2$	$ZrSn_2$	FeSn	-	Fe	520	79
15	$LaNi_2Sn$	$LaSn_3$	Ni_3Sn_2, Ni_3Sn	-	-	480	88
16	$PdCu_2Sn$	$PdSn_2$	Cu_3Sn	-	Cu	480	97
17	CuSn	Cu_6Sn_5	Cu_3Sn	Sn(β)	-	520	94
18	Fe_3Sn_2	FeSn	Fe_3Sn	Sn(β)	-	480	85
19	$FeNiSn_2$	NiSn	FeSn, Ni_3Sn	-	-	720	83
20	Ti_2Sn_3	Ti_6Sn_5	Ti_6Sn_5, Ti_2Sn	-	-	840	80
21	TiSn	Ti_6Sn_5	Ti_2Sn	Sn(β)	-	880	84
22	Cu_6Sn_5	Cu_6Sn_5	Cu_3Sn	-	-	670	90
23	CuSn	Cu_6Sn_5	Cu_3Sn	Sn(β)	-	720	86
24	FeCuSn	Cu_6Sn_5	Cu_3Sn, Fe_3Sn	-	-	550	82
25	Fe_2CuSn	Cu_6Sn_5	Cu_3Sn, Fe_3Sn	-	-	580	87

[0042]

[Table 2]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] (mAh/g)	[illegible] (%)
26	Fe_2CoSn	Co_3Sn_2	$CoSn$	-	Fe_3Sn	520	85
27	$TiFeSn$	Ti_6Sn_5	Ti_2Sn, Fe_3Sn	-	-	500	81
28	Ti_2Sn	Ti_6Sn_5	Ti_3Sn	-	-	530	86
29	$Ti_{10}Sn$	Ti_6Sn_5	Ti_3Sn	Sn(4)		520	84
30	Mg_2FeSn_2	Mg_2Sn	Fe_3Sn	-	Mg	710	85
31	[illegible]	K_2Sn	Mg_2Sn	Sn(2)	-	550	88
32	$CuCr_2Sn$	Cu_6Sn_5	Cu_3Sn	-	-	520	91
33	CaSi	$CaSi_2$	Ca_2Si	-	-	750	84
34	TiSi	$TiSi_2$	TiSi, Ti_5Si_3	-	-	710	86
35	Zr_2Si	$ZrSi_2$	ZrSi	Si(4)	-	700	85
36	V_5Si_3	VSi_2	V_3Si	-	-	840	85
37	NbSi	$NbSi_2$	Nb_5Si_3	-	Nb	550	81
38	Mo_5Si_3	$MoSi_2$	Mo_3Si	-	Mo	620	85
39	W_5Si	WSi_2	W_5Si_3	-	W	520	84
40	MnSi	$MnSi_2$	MnSi, Mn_3Si	-	-	560	87
41	FeSi	$FeSi_2$	FeSi, Fe_5Si_3	Si(1)	Fe	530	84
42	Fe_5Si_3	$FeSi_2$	FeSi, Fe_3Si	Si(2)	-	600	82
43	CoSi	$CoSi_2$	CoSi, Co_2Si	Si(2)	-	500	86
44	Co_2Si	$CoSi_2$	CoSi, Co_2Si, Co_3Si	-	-	570	83
45	NiSi	$NiSi_2$	NiSi	Si(1)	-	730	78
46	Ni_2Si	$NiSi_2$	NiSi, Ni_3Si_2	-	-	550	89
47	CuSi	$CuSi_2$	Cu_5Si_3	-	Cu	680	85
48	Ti_2CoSi_2	CoSi, TiSi	Ti_5Si_3	-		580	87
49	Ti_5Si	TiSi	Ti_5Si_3	Si(4)	-	620	84
50	Cr_3Si	CrSi	Cr_3Si	Si(1)	-	600	88

[0043]

[Table 3]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] (mAh/g)	[illegible] (%)
51	Fe_2Si	FeSi	Fe_3Si_7	-	-	880	92
52	FeMnSi	FeSi	Mn_5Si	Si(3)	-	910	88
53	Mn_3Si	MnSi	Mn_5Si_3, Mn_3Si	-	-	880	93
54	NiFeSi	FeSi	Fe_3Si_7	-	Ni	900	91
55	Mn_5Si	Mn_5Si_3	Mn_3Si	-	-	840	96
56	Co_2Si	Co_2Si	Co_3Si	Si(3)	-	820	93
57	$CaCoAl_2$	$CaAl_4$, $CoAl_2$	CoAl	-	-	730	73
58	$CaAl_2$	$CoAl_2$	CaAl, Ca_3Al_2	-	-	920	77
59	$CoAl_2$	$CuAl_2$	CoAl, Co_3Al_2	-	-	720	75
60	$FeAl_2$	$FeAl_2$	FeAl	-	-	780	72
61	$TiAl_2$	$TiAl_3$	TiAl	Al(3)	-	750	76
62	$MnAl_2$	$MnAl_3$	MnAl	-	-	700	73
63	$LaAl_2$	LaAl	La_3Al_2	-	-	820	83
64	FeAl	FeAl	Fe_3Al	Al(3)	-	880	84
65	CuAl	CuAl	Cu_9Al_4	Al(3)	-	920	79

[0044] Moreover, the state of A ** in the section of the obtained active material particles and B ** was as follows. That is, any active material has the interface which A ** and B ** contacted, and 50weight % or more of A ** was distributing it, where B ** is contacted into the matrix of B **.

[0045] The examination cell which uses said active material for **** material, and is shown in drawing 1 was produced. To 7.5g of powder of said active material, 2g of graphite powder was mixed as an electric conduction agent. 0.5g of polyethylene powder was mixed as a binder, and it was considered as the medical mixture. Pressurization molding was carried out, and 0.1g of this medical mixture was 17.5mm in diameter with the electrode 1, and was installed into the case 3. The microporous polypropylene separator 7 was placed on the electrode. It poured in on the separator by making the mixed solution of 1:1 into nonaqueous electrolyte by the volume ratio of ethylene carbonate and dimethoxyethane which dissolved perchloric acid lithium (LiClO4) so that it might become in 1. and 1mol /. Besides, metal lithium 4 17.5mm in diameter was stuck inside, the obturation board 6 which attached the polypropylene gasket 5 to the perimeter part was placed and obturated, and it was considered as the examination cell. In addition, two show the current collection object of an electrode 1 among drawing 1, and 5 shows the current collection object of metal lithium.

[0046] Cathode polarization is carried out until an electrode 1 is set to 0V to the lithium

opposite poles by 0.5mA constant current about this examination cell (when seeing an active material electrode as ****), it is equivalent to charge. Anode polarization was carried out until the electrode was set to 1.8V next (when seeing an active material electrode as ****, it is equivalent to electric discharge). Then, cathode polarization and anode polarization were repeated. The first time electric discharge capacity per 1g of active materials at this time is shown in Tables 1-3. Next, the examination cell was decomposed, and when the electrode 1 after 10 cycle ********** was taken out and after cathode polarization and cathode polarization, and anode polarization were observed, the deposit (DENDO light) of metal lithium in an electrode surface was not seen.

[0047] Next, in order to evaluate the cycle characteristic of a battery of having used said active material for ****, the cylindrical battery shown in drawing 2 was produced. LiMn1.8Co0.2O4 which are a plus terminal active material mixed Li2CO3, Mn3O4, and Co3O4 by the predetermined molar ratio, and they compounded them by heating at 900 degrees C. Furthermore, what carried out the part class of this to 100 or less meshes was made into the plus terminal active material. To 100g of plus terminal active materials, water DISPAION of Poli ethylene tetrafluoride was added for carbon powder as an electric conduction agent, 8g and pure water were added by the resinous principle as 10g and a binder, and it was made the shape of a paste, and it applied to the core material of titanium, it dried and rolled, and the plus terminal board 11 was obtained.

[0048] Next, it mixed with said each active material by the bulk density as an electric conduction agent, the fluoro-resin (Teflon) binder was mixed with graphite powder at a rate of 70:20:10 as a binder, and it was made the shape of a paste using the oil system solvent, applied to the copper core material, and dried at 100 degrees C, and the negative polar plate 12 was obtained.

[0049] The band-like separator 13 whose width is wider than a two-poles board was made to intervene between the core material attached by spot welding, the plus terminal board 11 which has the plus terminal lead 14 of this quality of the material, the core material attached by spot welding, and the negative polar plate 12 which has the **** lead 15 of this quality of the material, and the whole was spirally wound around it. The up electric insulating plate 16 and the lower electric insulating plate 17 made from polypropylene were arranged on each upper and lower sides of the winding thing, and it inserted in **** 18. After making a step form in the upper part of **** 18, as nonaqueous electrolyte, the mixed solution of 1:1 was poured in by the volume ratio of ethylene carbonate and dimethoxyethane which dissolved perchloric acid lithium so that it might become in 1 and 1mol /, and it sealed with the obturation board 19, and the battery was completed. Porous polypropylene was used for the separator 13. In addition, 20 show a plus terminal terminal among drawing 2 .

[0050] About the obtained battery, charge and discharge current 1mA/cm2 were performed.

with the test temperature of 20 degrees C, and the charge-and-discharge cycle examination was done in the charge-and-discharge-voltage ranges 4.3-2.8V. The capacity maintenance rate of the 100 cycle eye to 1 cycle eye is shown in Tables 1-3.

[0051] <<Comparative examples 1-7>> The particles of Sn simple substance shown in Table 4, and aluminum simple substance (average particle diameter of 25 micrometers). The particles which consist only of Cu6Sn5 **, the particles which consist only of FeAl ** (all / average particle diameter of 28 micrometers) The particles which consist of the average particle diameter of 2.1 micrometers, and Mg2germanium ** and Mg element phase of a crystal grain ([average particle diameter of 25 micrometers]) The average particle diameter of 3.2 micrometers of a crystal grain and Mg2 germanium:Mg 7:3 (molar ratio), The particles which consist of Mg2Sn ** and a Mg element phase ([the average particle diameter of 27 micrometers, and average particle diameter of 5.3 micrometers of a crystal grain]) (Mg2 Sn:Mg / case / where the particles (the average particle diameter of 27 micrometers, the average particle diameter of 5.2 micrometers of a crystal grain, and Mg2 Sn:Sn are 7:3 (molar ratio)) which consist of 8:2 (molar ratio), Mg2Sn **, and Sn ** are used) It asked for the first time electric discharge capacity of an examination cell, and the capacity maintenance rate of the 100 cycle eye to 1 cycle eye of a cylindrical battery like the case of a work example. These results are shown in Table 4.

[0052]

[Table 4]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] (mAh/g)	[illegible] (%)
1	Sn	-	-	Sn(100)	-	880	12
2	Al	-	-	Al(100)	-	730	5
3	Cu_6Sn_5	Cu_6Sn_5	-	-	-	550	34
4	FeAl	FeAl	-	-	-	300	29
5	Mg_2Ge/Mg	Mg_2Ge	-	-	Mg	530	22
6	Mg_2Sn/Mg	Mg_2Sn	-	-	Mg	480	23
7	Mg_2Sn/Sn	Mg_2Sn	-	Sn(30)	-	650	20

[0053] the battery which used the active material concerning this invention for *** is high capacity compared with a comparative example, and Tables 1-4 show that the cycle characteristic is markedly alike and improves. In addition, in said work example, although the cylindrical battery was produced, it is checking that the same effect is acquired also in a coin type, a square shape, and a flat rechargeable battery. Moreover, in said work example, although the gas atomizing method was adopted, even if it adopts the plasma method, a rapid

coating method, a casting process, the mechanical alloy method, and the mechano-chemical method, it is checking that the same effect is acquired. Moreover, in said work example, although LiMn1.8Co0.2O4 were used as a plus terminal, also when LiMn2O4, LiCoO2, LiNiO2, etc. are used, it is checking that the same effect is acquired.

[0054]

[Effect of the Invention] According to this invention, there is no short circuit according to a DENDO light at high energy density, and the nonaqueous electrolyte rechargeable battery excellent in cycle length can be obtained.

[Brief Description of the Drawings]

[Drawing 1] In order to evaluate the characteristic of the **** active material of this invention, it is the cross-sectional schematic view of an examination cell used in the work example.

[Drawing 2] In order to evaluate the characteristic of the **** active material of this invention, it is the cross-sectional schematic view of the cylindrical battery used in the work example.

[Explanations of letters or numerals]

1 Electrode

2 Current Collection Object of Electrode 1

3 Case

4 Metal Lithium

5 Current Collection Object of Metal Lithium

6 Obturation Board

7 Microporous Polypropylene Separator

8 Gasket

11 Plus Terminal Board

12 Negative Poter Plate

13 Separator

14 Plus Terminal Lead

15 **** Lead

16 Up Electric Insulating Plate

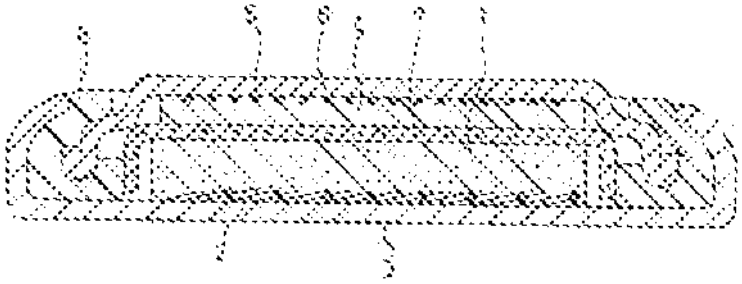
17 Lower Electric Insulating Plate

18 ****

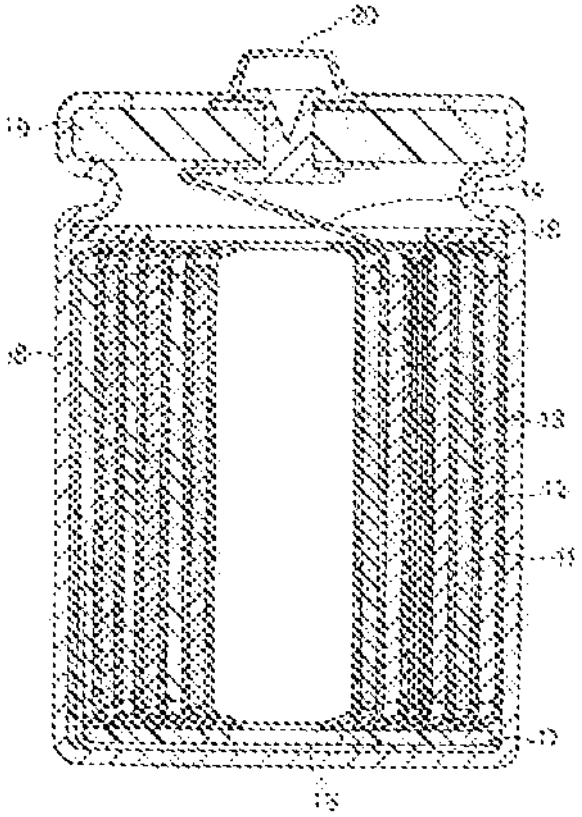
19 Obturation Board

20 Plus Terminal Terminal

[Drawing 1]



[Drawing 2]



[Translation done.]